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AZO DYE OF A 3-AMINOPHTHALIMIDE AND CONTAINING CARBAMOYL MOIETIES

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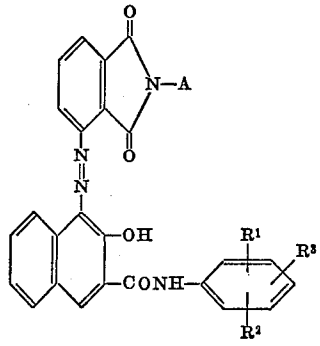
U.S. Cl. 260—152 3 Claims

ABSTRACT OF THE DISCLOSURE

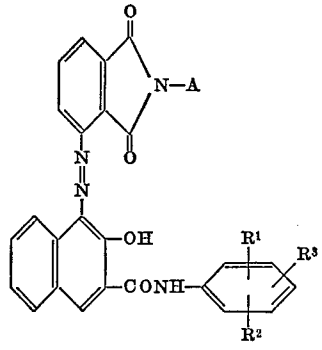
This invention is directed to monoazo pigments of the formula of



(1)

in which R^1 denotes carbamoyl among other possible constituents; R^2 and R^3 denote hydrogen or chlorine among other possible constituents; and A denotes phenyl among other constituents. The pigments generally have red shades and are eminently suitable for example for coloring lacquers, resins and printing inks.

The invention relates to dyes of the general formula (1)



(1)

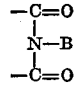
in which

R^1 denotes carbamoyl, carbamoyl bearing aryl as a substituent or amino bearing a C-acyl or a substituted C-acyl group as a substituent on the nitrogen atom;

R^2 denotes hydrogen, chlorine, bromine, alkoxy, cyano, carbomethoxy, methyl sulfonyl, carbamoyl or carbamoyl bearing aryl as a substituent;

R^3 denotes hydrogen, chlorine, methyl or alkoxy,

R^1 and R^2 together may denote the radical of the formula:

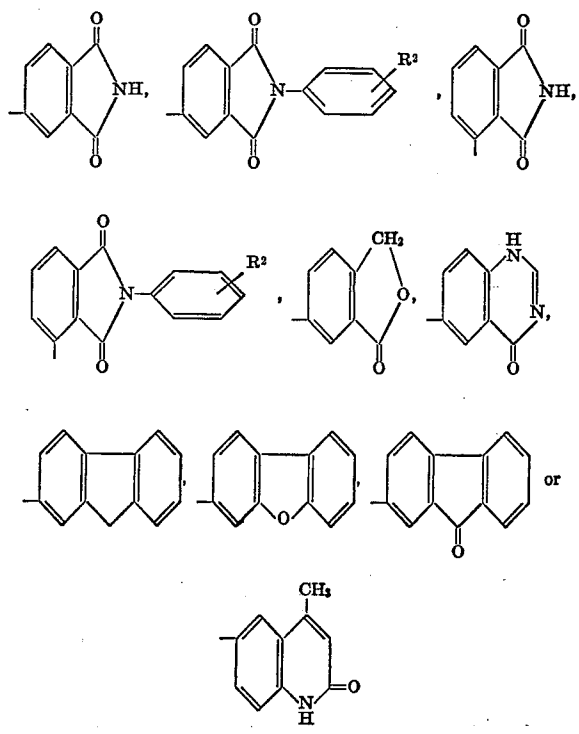


A denotes phenyl, naphthyl, diphenyl, fluorenyl or anthraquinonyl which may bear chloro, cyano, alkyl, alkoxy or carboalkoxy as a substituent; and

B denotes a hydrogen atom or aryl of one to three rings which may be substituted and may contain ring heteroatoms.

Alkoxy radicals for R^2, R^3 or A include for example methoxy and ethoxy. Alkyl and carboalkoxy radicals for A include for example methyl, ethyl, carbomethoxy and carboethoxy.

Examples of radicals B (other than hydrogen) are methyl, phenyl, or phenyl, naphthyl or anthraquinonyl bearing, as substituents, chlorine, bromine, methyl, ethyl, methoxy, ethoxy, phenoxy, chlorophenoxy, phenyl, benzoyl, cyano, carbomethoxy, carbamoyl, sulfonamido, acetylamino, benzoylamino, chlorobenzoylamino, methylbenzoylamino or nitro, and also the radicals having the formula:

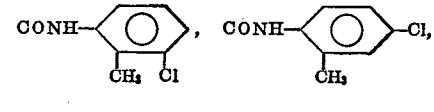


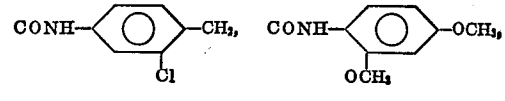
Preferred radicals B include for example phenyl, or phenyl or naphthyl bearing, as substituents, chloro, methyl, ethyl, methoxy, ethoxy, phenyl, carbomethoxy, carbamoyl, sulfonamido, acetylamino, benzoylamino or methylbenzoylamino.

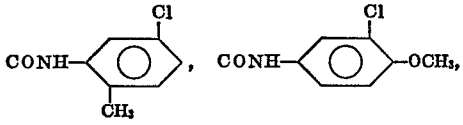
R^2 has the meanings given above.

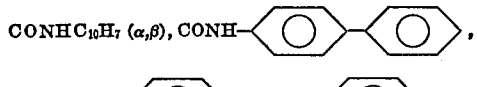
Examples of radicals R^1 are:

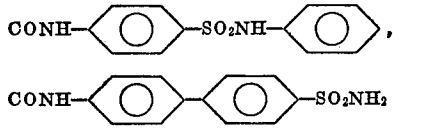
$CONH_2$, $CONHCONH_2$, $CONHC_6H_5$, $CONHC_6H_4Cl$ (o,m,p), $CONHC_6H_4CH_3$ (o,m,p), $CONHC_6H_4OCH_3$ (o,m,p), $CONHC_6H_4Br$ (o,m,p), $CONHC_6H_4SO_2NH_2$ (o,m,p), $CONHC_6H_3Cl_2$ (2,4; 3,4; 2,5; 3,5)



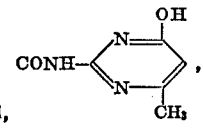


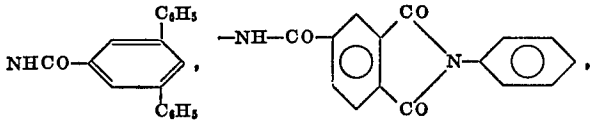


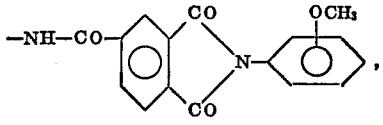


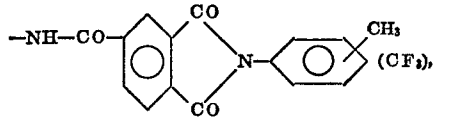


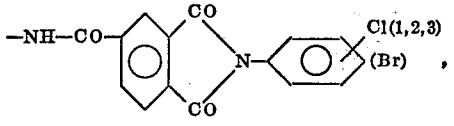
CONH—anthraquinonyl (α,β),
CONH—3—chloroanthraquinonyl-(β),
$NHCOC_6H_5$, $NHCOC_6H_4Cl$(o,m,p),
$NHCOC_6H_3Cl_2$(2,4; 2,5),
$NHCOC_{10}H_7$ (α,β), NHCO—anthraquinonyl,

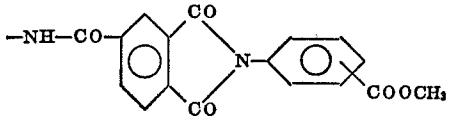


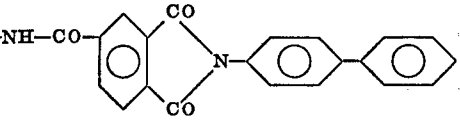


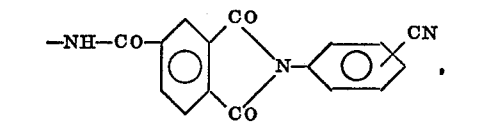


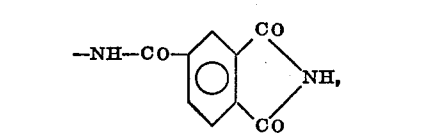


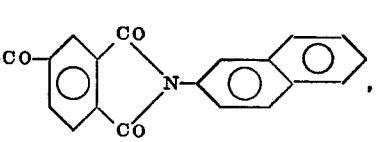


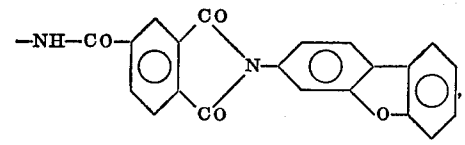


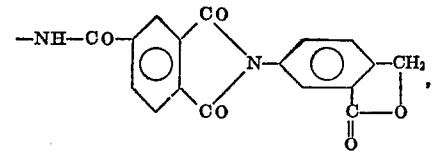


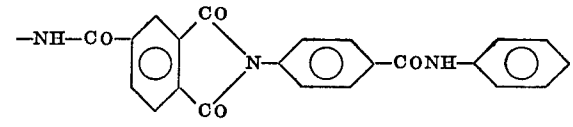












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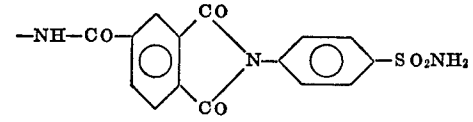
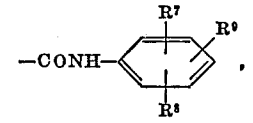
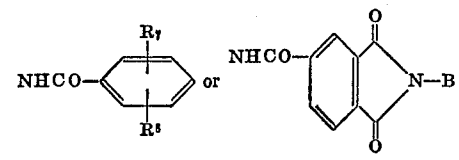


Preferred radicals R^1 have the formula:



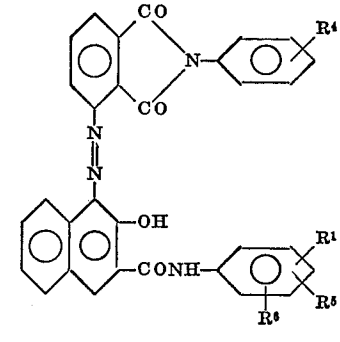


in which

R^7 denotes hydrogen, fluoro, chloro, methyl, ethyl, methoxy, ethoxy, carbomethoxy, carbamoyl, sulfonamido, N-phenylsulfonamido or cyano;
R^8 denotes hydrogen, chloro, methyl, methoxy or ethoxy;
R^9 denotes hydrogen, chloro, methyl or methoxy; and
B has the above meanings.

N - phenylcarboxamide, N - chlorophenylcarboxamide, N-methylphenylcarboxamide, N-methoxyphenylcarboxamide and N-dichlorophenylcarboxamide are suitable as aryl-substituted carboxamides for R^2.

Dyes of the general formula (1a) are preferred:

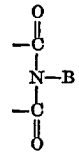


(1a)

in which

R^4 denotes hydrogen, chloro, methyl, ethyl, methoxy ethoxy or phenyl;
R^5 denotes hydrogen, chloro, cyano, methyl or methoxy;

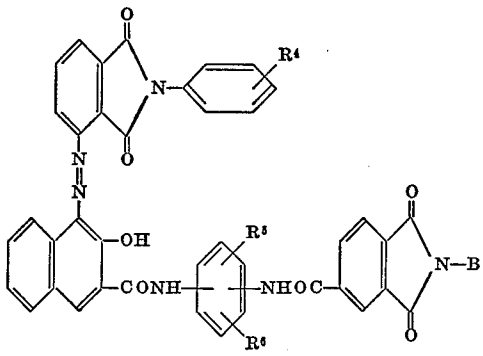
R^6 denotes hydrogen, chloro, methyl or methoxy; and R^1 and R^5 together may denote the radical of the formula:



in which R^1 and B have the above meanings.

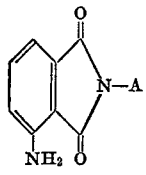
The radical of the said formula (R^1+R^5) is preferably in the 3,4-position to the —CO—NH— group.

Another group of valuable pigments has the general formula (1b):



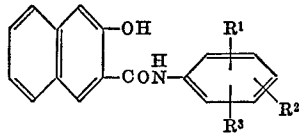
in which B, R^4, R^5 and R^6 have the above meanings.

For the production of the compounds of formula (1), a diazo compound of an amine of formula (2):



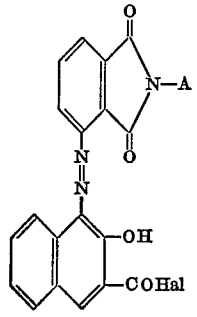
(2)

may be reacted with a coupling component of formula (3):

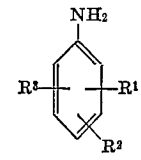


(3)

An azo compound of formula (4)



in which Hal denotes bromine or, preferably, chlorine may be condensed with an amine of the general formula (5)



(5)

The compounds of formula (4) may be prepared by reaction of the diazo compound of an amine of formula (2) with β-hydroxynaphthoic acid followed by halogenation.

Examples of compounds of formula (2) are:

N-phenyl-3-aminophthalimide,
N-2'-chlorophenyl-3-aminophthalimide,
N-3'-chlorophenyl-3-aminophthalimide,
N-4'-chlorophenyl-3-aminophthalimide,
N-2'-methylphenyl-3-aminophthalimide,
N-3'-methylphenyl-3-aminophthalimide,
N-4'-methylphenyl-3-aminophthalimide,
N-2'-methoxyphenyl-3-aminophthalimide,
N-3'-methoxyphenyl-3-aminophthalimide,
N-4'-methoxyphenyl-3-aminophthalimide,
N-2'-carbomethoxyphenyl-3-aminophthalimide,
N-3'-carbomethoxyphenyl-3-aminophthalimide,
N-4'-carbomethoxyphenyl-3-aminophthalimide,
N-2',4'-dichlorophenyl-3-aminophthalimide,
N-2',5'-dichlorophenyl-3-aminophthalimide,
N-3',4'-dichlorophenyl-3-aminophthalimide,
N-2',5'-dicarbomethoxyphenyl-3-aminophthalimide,
N-2',4'-dimethylphenyl-3-aminophthalimide,
N-2',5'-dimethylphenyl-3-aminophthalimide,
N-3',4'-dimethylphenyl-3-aminophthalimide,
N-3'-chloro-4'-methylphenyl-3-aminophthalimide,
N-4'-chloro-3'-carbomethoxyphenyl-3-aminophthalimide,
N-2'-chloro-4'-methoxyphenyl-3-aminophthalimide,
N-β-naphthyl-3-aminophthalimide,
N-(4'-phenyl)-phenyl-3-aminophthalimide,
N-3'-fluorenyl-3-aminophthalimide, or
N-β-anthraquinonyl-3-aminophthalimide.

The following are suitable amines of the formula (5):

3-benzoylaminoaniline,
4-benzoylaminoaniline,
3-chlorobenzoylaminoaniline,
4-chlorobenzoylaminoaniline,
3-dichlorobenzoylaminoaniline,
4-dichlorobenzoylaminoaniline,
3-chloromethoxybenzoylaminoaniline,
4-chloromethoxybenzoylaminoaniline,
3-methoxybenzoylaminoaniline,
4-methoxybenzoylaminoaniline,
3-methylbenzoylaminoaniline,
4-methylbenzoylaminoaniline,
3-α-naphthoylaminoaniline,
4-α-naphthoylaminoaniline,
3-β-naphthoylaminoaniline,
4-β-naphthoylaminoaniline,
3-β-anthraquinonocarbonylaminoaniline,
4-β-anthraquinonocarbonylaminoaniline,
3-trichlorobenzoylaminoaniline,
4-trichlorobenzoylaminoaniline,
3-methoxy-4-benzoylaminoaniline,
3-methoxy-4-β-naphthoylaminoaniline,
3-methoxy-4-dichlorobenzoylaminoaniline,
3-methyl-4-benzoylaminoaniline,
3-methyl-4-β-naphthoylaminoaniline,

2-methoxy-4-benzoylaminoaniline,
2-methoxy-4-trichlorobenzoylaminoaniline,
2-methoxy-4-β-naphthoylaminoaniline,
2-methoxy-5-chloro-4-benzoylaminoaniline,
2-methoxy-5-chloro-4-β-naphthoylaminoaniline
2-methyl-4-benzoylaminoaniline,
2-methyl-4-β-naphthoylaminoaniline,
2-methyl-4-chloro-5-benzoylaminoaniline,
3-aminobenzoic acid chloroanilide,
4-aminobenzoic acid chloroanilide,
3-aminobenzanilide,
4-aminobenzanilide,
3-aminobenzodichloroanilide,
4-aminobenzodichloroanilide,
3-aminobenzo-β-naphthylamide,
4-aminobenzo-β-naphthylamide,
3-aminobenzoyl-α-aminoanthraquinone,
4-aminobenzoyl-α-aminoanthraquinone,
3-aminobenzotrichloroanilide,
4-aminobenzotrichloroanilide,
3'-aminobenzoyl-4-aminodiphenyl,
4'-aminobenzoyl-4-aminodiphenyl,
N-phenyl-4-aminophthalimide,
4-aminophthalimide,
N-(4'-chloro)-phenyl-4-aminophthalimide,
N-(2'-chloro)-phenyl-4-aminophthalimide,
N-(2',4'-dichloro)-phenyl-4-aminophthalimide,
N-(2'-carboxymethyl)-phenyl-4-aminophthalimide,
N-(4'-methoxy)-phenyl-4-aminophthalimide,
N-phenyl-3-aminophthalimide, and
3-aminophthalimide.

Compounds of formula (4) are obtained by conventional methods from the appropriate carboxylic acid by reaction with halogenating agents such as $POCl_3$, $SOCl_2$ or $COCl_2$, preferably in an inert solvent such as nitrobenzene, a halobenzene or a xylene with the addition of a catalytic amount of dimethylformamide or pyridine.

Condensation of the azocarboxylic chlorides or bromides of formula (4) with the amines of formula (5) is advantageously carried out by heating in organic solvents such as o-dichlorobenzene, nitrobenzene, methyl benzoate, xylene, dimethylformamide or N-methylpyrrolidone, and acid-binding agents or a catalytic amount of a compound such as collidine or N-methylpyrrolidone may be added which accelerate the reaction at temperatures of more than 100° C.

The coupling component of formula (3) may be prepared for example by condensation of 2-hydroxynaphthalene-3-carboxylic acid chloride with an amine of formula (5) or by condensation of 2-hydroxynaphthoic acid (3) with an amine of formula (5) in the presence of a chlorinating agent such as PCl_3.

Coupling of the compounds of formula (3) is advantageously carried out by bringing the aqueous alkaline solution of the coupling component or a very finely divided suspension of the coupling component in water together with the acid diazo solution. A pH range of from 4 to 7 is adjusted (advantageously by adding a buffer such as sodium acetate) and the addition of wetting or dispersing agents, for example aralkyl sulfonates, makes for a uniform course of the reaction. The new dyes may also be prepared by the modified process of French Pat. No. 1,537,423.

The pigments of the invention are obtained in this way in a very pure chemical condition but occasionally not in the optimum physical form for all applications. They may be brought into the form adapted to the particular application by conventional measures such as size reduction, salt grinding or recrystallization.

The new pigments may be used for dope dyeing for example of viscose, for the production of colored print pastes for book or offset printing, for the production of colored surface coatings, for example nitrocellulose lacquers, acrylate lacquers, melamine resin lacquers or alkyd resins, for dyeing phenoplasts or aminoplasts or thermoplastics such as polystyrene, polyolefins or polyvinyl chloride, rubber or silicone resins, for dyeing laminate papers or boards and for textile printing.

The new pigments are particularly suitable for dyeing polyvinyl chloride, polyethylene or polypropylene and in coating compositions and high grade printing inks.

The following Examples illustrate the invention. Unless otherwise stated the parts and percentages are by weight; the temperatures are given in degrees C.

EXAMPLE 1

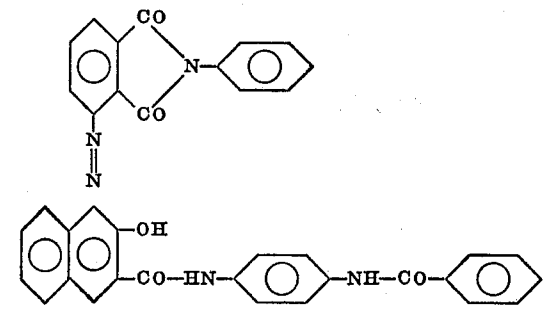
288 parts of the dye obtained by coupling diazotized N-phenyl-3-aminophthalimide with 2-hydroxynaphthoic acid-3 is heated with 2600 parts of o-dichlorobenzene, 260 parts of thionyl chloride and 8 parts of dimethylformamide at 110° to 120° while stirring for five hours.

After the reaction mixture has cooled, the uniformly crystalline azo dye monocarboxylic acid chloride is isolated by suction filtration, washed with 200 parts of o-dichlorobenzene, then with 1000 parts of benzene and then with 1000 parts of cyclohexane and dried at 80° at subatmospheric pressure. 266 parts of a red crystal powder is obtained.

Analysis.—Calculated: Cl=7.8%. Found: Cl=7.6%.

22.8 parts of the azo dye carboxylic acid chloride thus obtained is stirred into 800 parts of dry o-dichlorobenzene, then 12.7 parts of finely powdered 4-benzoylaminoaniline and 5 parts of dimethylformamide are added and the whole is then heated for five hours at 140° to 150°. After cooling the whole to 80° the deposited sparingly soluble pigment is suction filtered and washed with a little hot o-dichlorobenzene and then with cold methanol until the filtrate running away is clear. The pigment can be improved by boiling it up with methanol or another solvent for two hours or stirring it at room temperature, preferably with N-methylpyrrolidone. After the product has been dried at 80° at subatmospheric pressure, 22.0 parts of a red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film and sheeting and lacquers are colored red shades having excellent fastness to light, migration and overcoating.

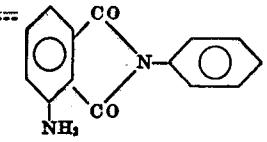
The pigment has the formula:



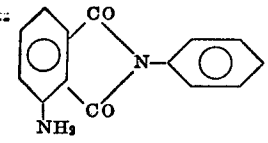
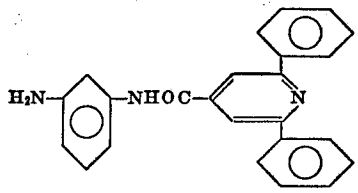
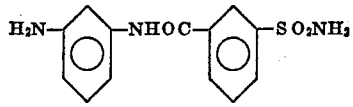
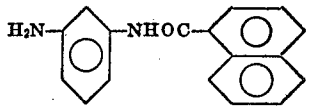
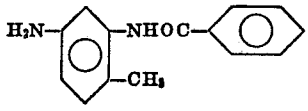
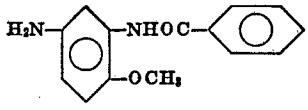
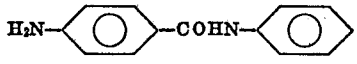
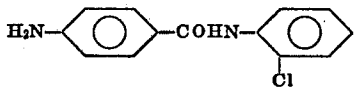
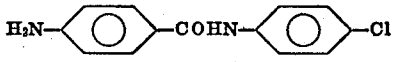
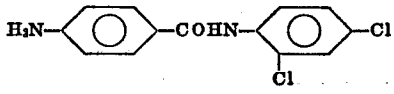
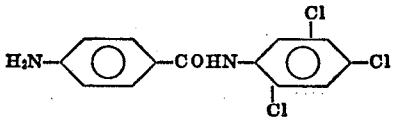
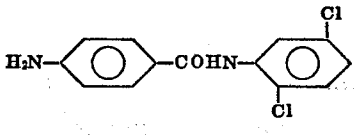
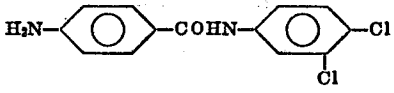
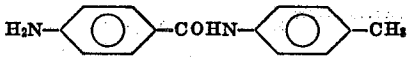
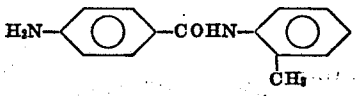
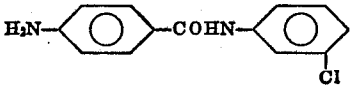
Analysis.—Calculated: N=11.1%. Found: N=11.3%.

Other monoazo pigments are obtained with the components in the following Table by coupling 1 mole of the diazo compound of the amine specified in column (I) onto 1 mole of 2-hydroxynaphthoic acid-(3), converting the resultant monoazo dye carboxylic acid into the acid chloride and condensing it with 1 mole of the amine specified in column (II).

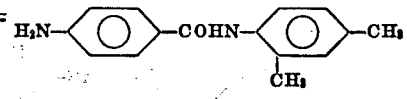
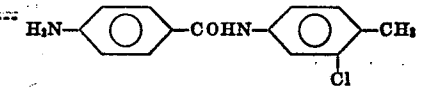
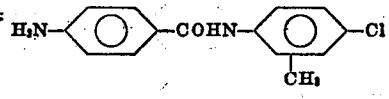
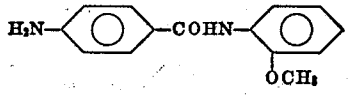
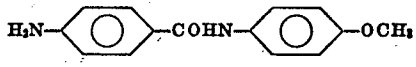
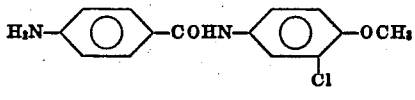
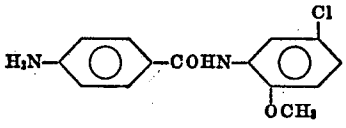
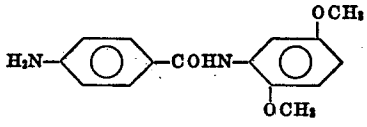
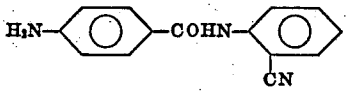
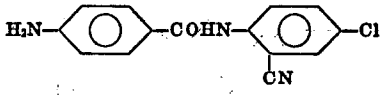
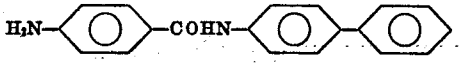
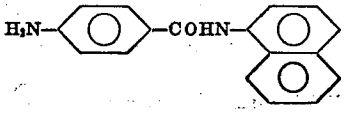
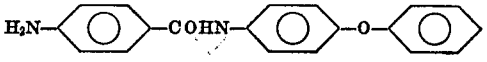
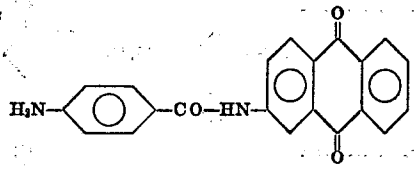
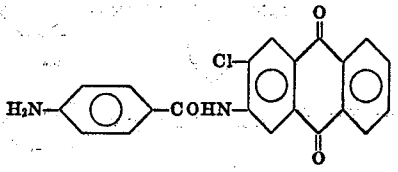
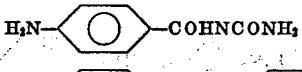
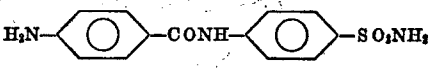
Column (III) indicates the shade of a lacquer coating prepared from the pigment obtained.

I	II	III
Example:		
2		Yellowish red.
3	Same as above	Red.
4	do	Red.
5	do	Red.
6	do	Red.
7	do	Red.
8	do	Red.
9	do	Red.
10	do	Red.
11	do	Brown.
12	do	Bluish red.
13	do	Yellowish red.
14	do	Do.
15	do	Do.
16	do	Do.

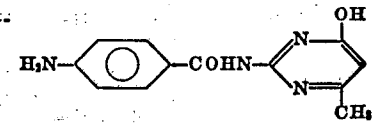
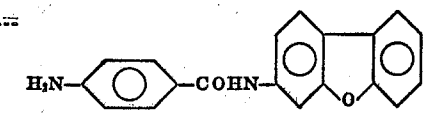
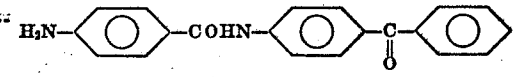
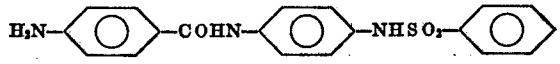
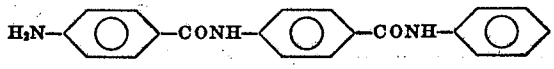
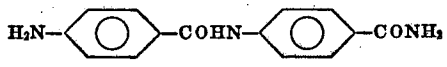
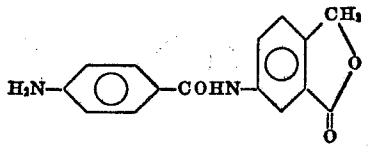
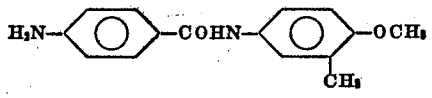
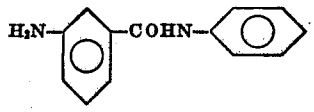
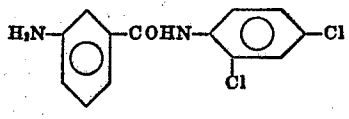
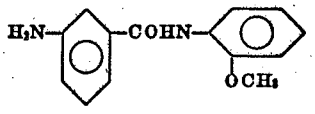
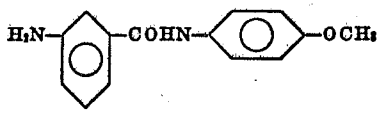
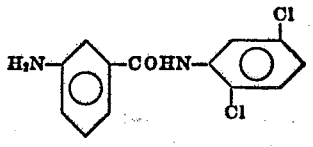
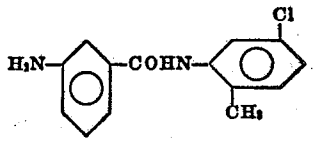
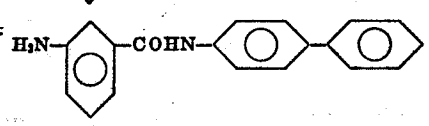
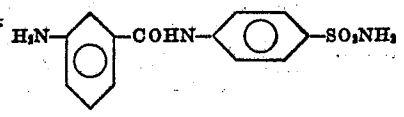
TABLE—Continued

I	II	III
Example:		
17		Yellowish red.
18 Same as above		Red.
19 do		Red.
20 do		Red.
21 do		Red.
22 do		Bluish red.
23 do		Yellowish red.
24 do		Do.
25 do		Do.
26 do		Orange red.
27 do		Red.
28 do		Bluish red.
29 do		Red.
30 do		Red.
31 do		Red.
32 do		Yellowish red.

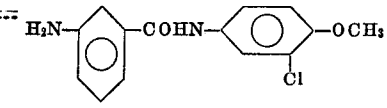
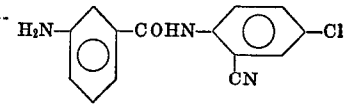
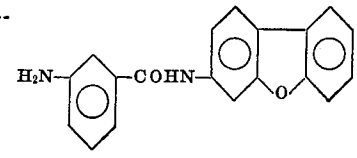
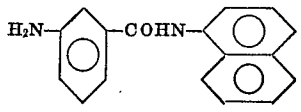
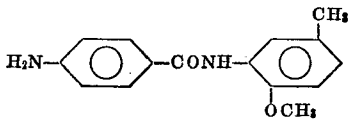
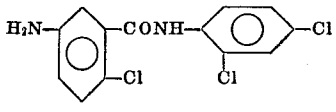
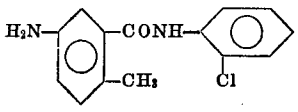
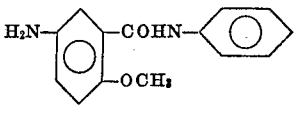
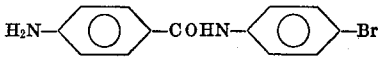
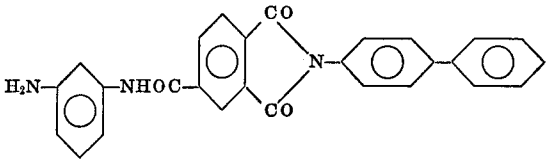
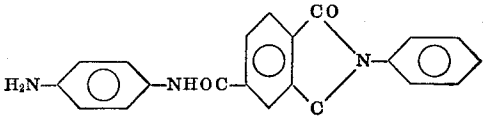
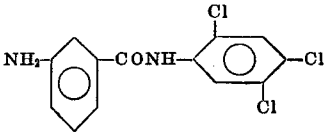
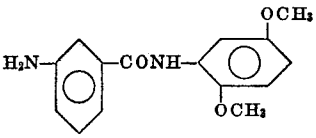
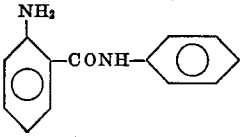
TABLE—Continued

I	II	III
Example:		
33 Same as Example 2		Red.
34 do		Red.
35 do		Yellowish red.
36 do		Red.
37 do		Red.
38 do		Yellowish red.
39 do		Red.
40 do		Red.
41 do		Yellowish red.
42 do		Do.
43 do		Do.
44 do		Do.
45 do		Do.
46 do		Red.
47 do		Yellowish red.
48 do		Do.
49 do		Do.

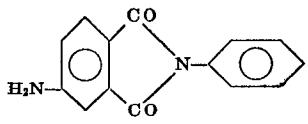
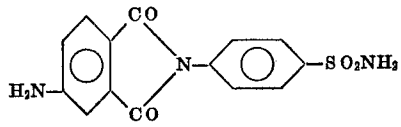
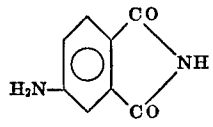
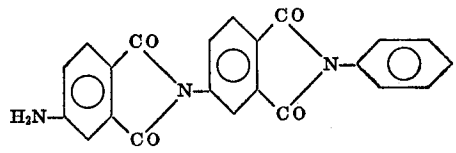
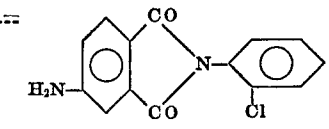
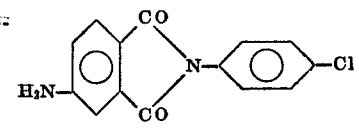
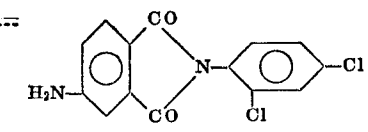
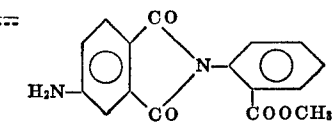
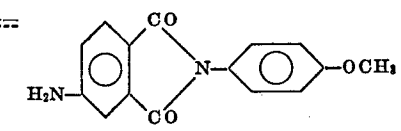
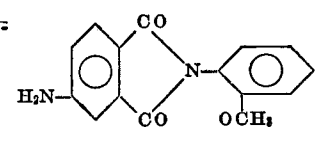
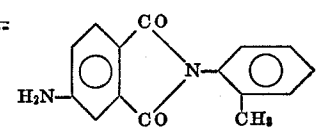
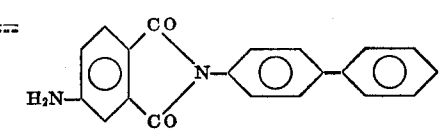
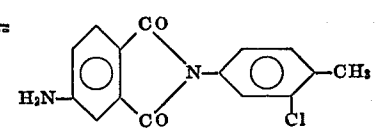
TABLE—Continued

I	II	III
Example: 50.... Same as Example 2		Yellowish red.
51.....do.....		Red.
52.....do.....		Yellowish red.
53.....do.....		Red.
54.....do.....		Yellowish red.
55.....do.....		Red.
56.....do.....		Red.
57.....do.....		Red.
58.....do.....		Yellowish red.
59.....do.....		Bluish red.
60.....do.....		Red.
61.....do.....		Yellowish red.
62.....do.....		Do.
63.....do.....		Do.
64.....do.....		Do.
65.....do.....		Red.

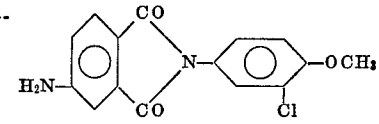
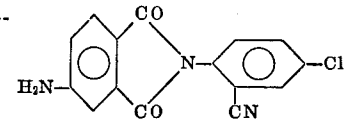
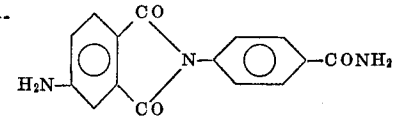
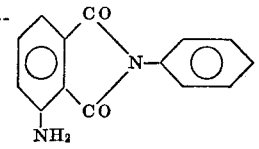
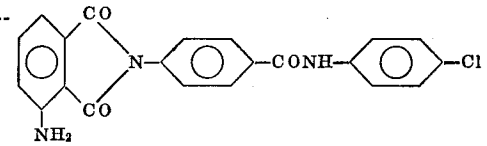
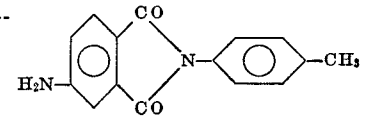
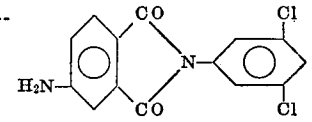
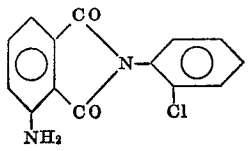
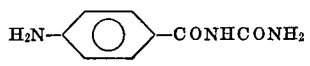
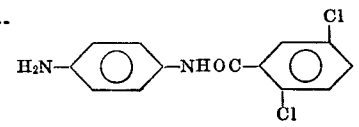
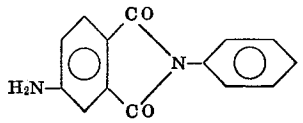
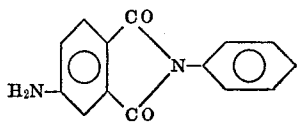
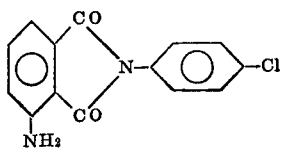
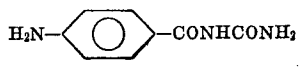
TABLE—Continued

I	II	III
Example: 66.... Same as Example 2		Red.
67.....do.....		Yellowish red.
68.....do.....		Red.
69.....do.....		Red.
70.....do.....		Yellowish red.
71.....do.....		Red.
72.....do.....		Red.
73.....do.....		Red.
74.....do.....		Red.
75.....do.....		Orange.
76.....do.....		Red.
77.....do.....		Yellowish red.
78.....do.....		Red.
79.....do.....		Yellowish red.

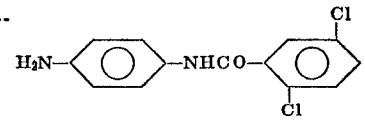
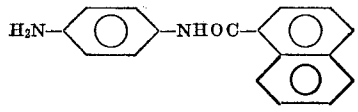
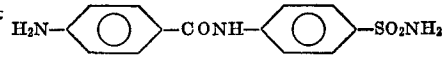
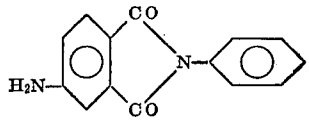
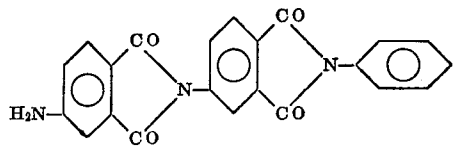
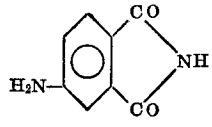
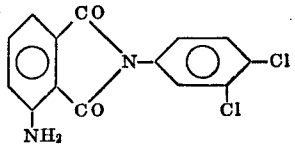
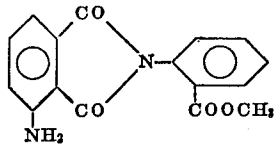
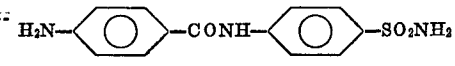
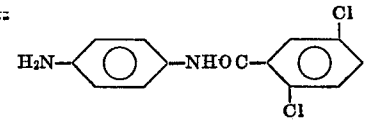
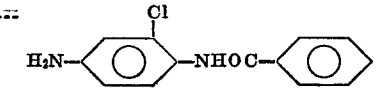
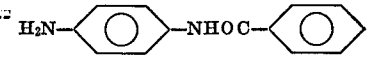
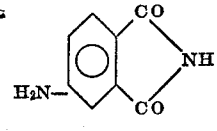
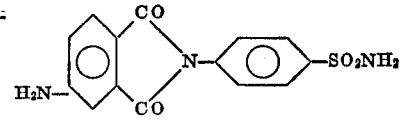
TABLE—Continued

I	II	III
Example 80.... Same as Example 2.....		Yellowish red.
81.....do.....		Red.
82.....do.....		Bluish red.
83.....do.....		Do.
84.....do.....		Yellowish red.
85.....do.....		Red.
86.....do.....		Bluish red.
87.....do.....		Red.
88.....do.....		Bluish red.
89.....do.....		Red.
90.....do.....		Yellowish red.
91.....do.....		Yellowish red.
92.....do.....		Yellowish red.

TABLE—Continued

I	II	III
Example:		
93 Same as Example 2		Red.
94 do		Yellowish red.
95 do		Red.
96 do		Orange red.
97 do		Orange.
98 do		Yellowish red.
99 do		Bluish red.
100 		Yellowish red.
101 Same as above		Red.
102 do		Yellowish red.
103 do		Bluish red.
104 		Yellowish red.

TABLE—Continued

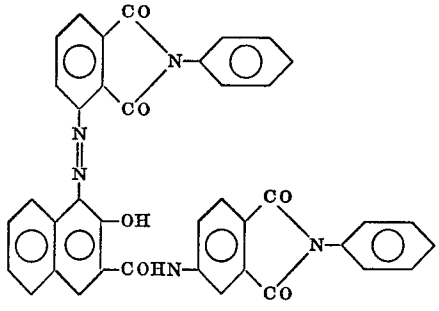
I	II	III
Example: 105 Same as Example 104		Red.
106 do		Reddish brown.
107 do		Yellowish red.
108 do		Brownish red.
109 do		Red.
110 do		Red.
111		Red.
112		Yellowish red.
113 Same as above		Red.
114 do		Red.
115 do		Red.
116 do		Yellowish red.
117 do		Red.
118 do		Yellowish red.

EXAMPLE 119

34.2 parts of the azo dye carboxylic acid chloride obtained according to Example 1 is stirred in 600 parts of N-methylpyrrolidone-(2), then 23.8 parts of finely powdered N-phenyl-4-aminophthalimide is added and the whole is heated for five hours at 140° to 150°. The sparingly soluble pigment thus precipitated in finely crystalline form is cooled to 80° and suction filtered, and washed with N-methylpyrrolidone-(2) and then with cold methanol until the filtrate running away is clear. The pigment can be improved by boiling it up for two hours in methanol or another solvent or stirring it at room temperature.

After drying at 80° at subatmospheric pressure 45.0 parts of a red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film, sheeting and coating compositions are colored therewith red shades having excellent fastness to light, migration and overcoating.

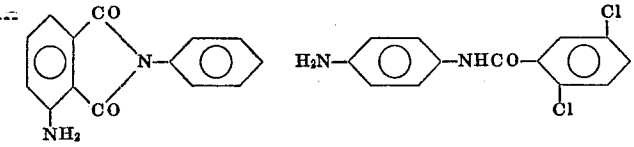
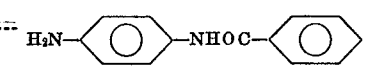
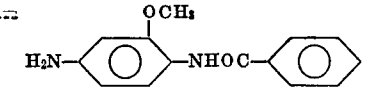
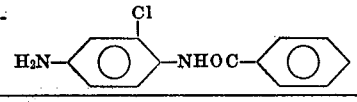
The pigment has the formula:



Analysis.—Calculated: N=10.7%. Found: N=10.6%.

Other monoazo pigments are obtained with the components in the following Table by coupling 1 mole of the diazo compound of the amines specified in column I with 1 mole of 2-hydroxynaphthoic acid-(3), converting the resultant monoazo dye carboxylic acid into its acid chloride and condensing this with 1 mole of the amine specified in column II.

Column III indicates the shade of a coating prepared with the pigment obtained.

I	II	III
Example number: 120		Red.
121 Same as above		Red.
122 do		Bluish red.
123 do		Red.

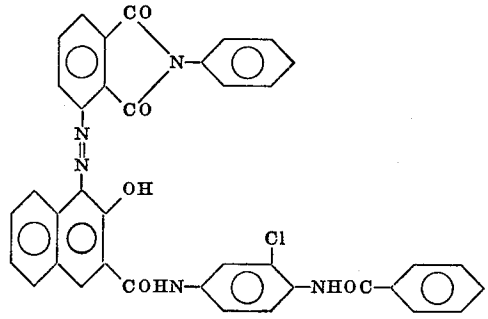
EXAMPLE 124

45.6 parts of the azo dye carboxylic acid chloride according to Example 1 is heated to about 80° in 1600 parts of dry o-dichlorobenzene. Then a hot solution of 29.6 parts of 3 - chloro - 4 - benzoylaminoaniline in 200 parts of N - methylpyrrolidone-(2) or dimethylformamide is added and the whole is heated for five hours at 140° to 150°.

The sparingly soluble pigment thus deposited in a finely crystalline form is cooled to 80°, suction filtered, and washed with a little o-dichlorobenzene or cold dimethylformamide or N - methylpyrrolidone-(2) and then with cold methanol until the filtrate running away is clear. The pigment may be improved by boiling it up with methanol or another solvent for another two hours or stirring it at room temperature.

After drying at 80° at subatmospheric pressure, 56.0 parts of a red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film, sheeting and coating compositions are colored therewith red shades of excellent fastness to light, migration and overcoating.

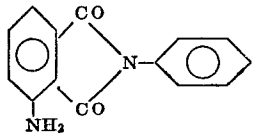
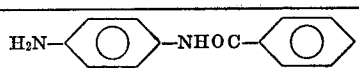
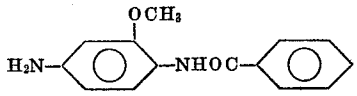
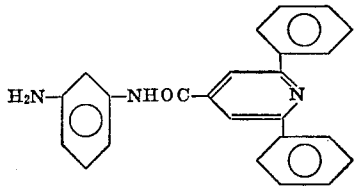
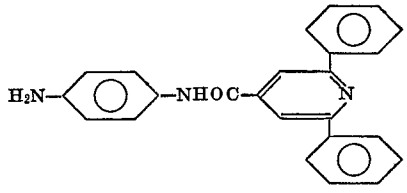
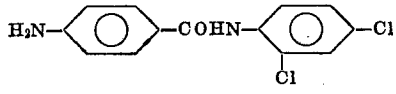
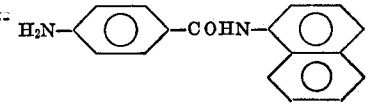
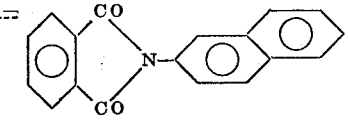
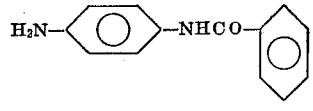
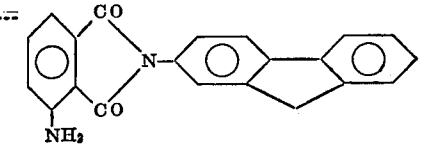
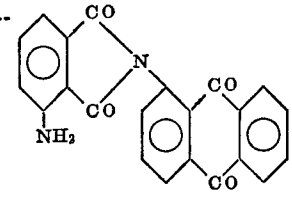
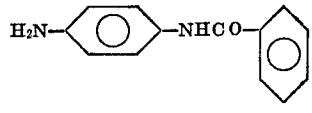
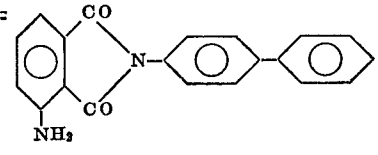
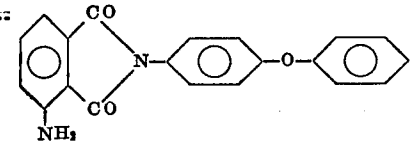
The pigment has the formula:



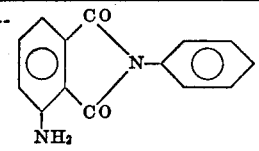
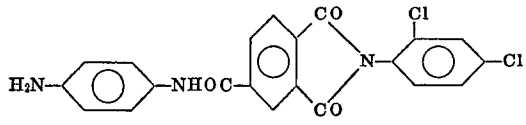
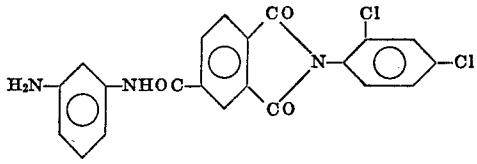
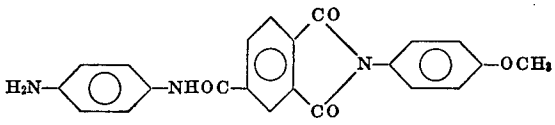
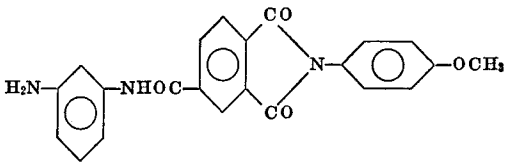
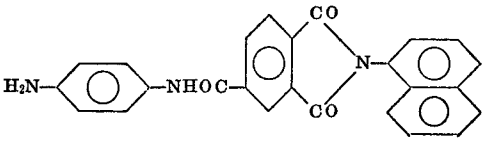
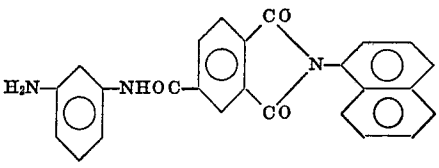
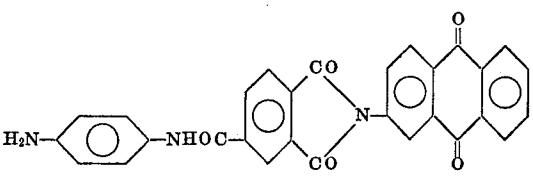
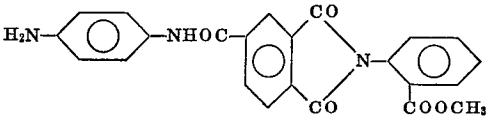
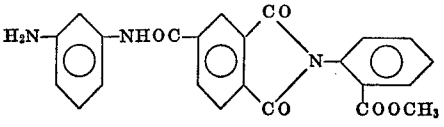
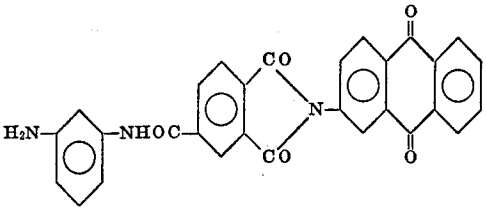
Analysis.—Calculated: N=10.5%. Found: N=10.7%.

Other monazo dyes are obtained with the components in the following Table by coupling 1 mole of the diazo compound of an amine specified in column I with 1 mole of hydroxynaphthoic acid-(3) and converting the monoazo dye carboxylic acid obtained into its acid chloride which is then condensed with 1 mole of an amine specified in column II.

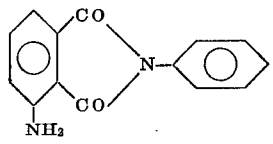
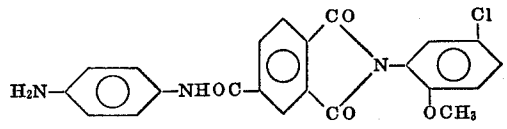
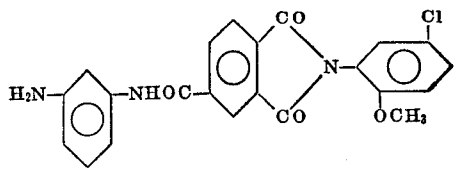
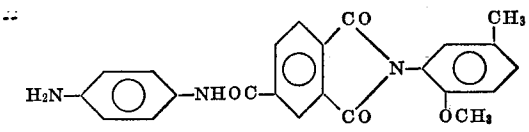
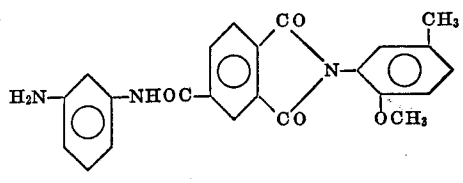
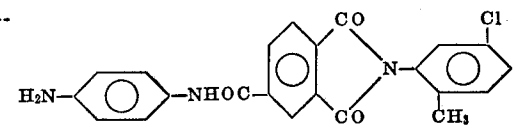
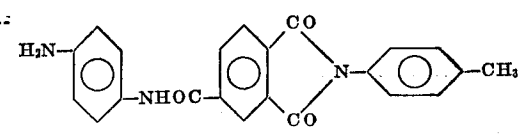
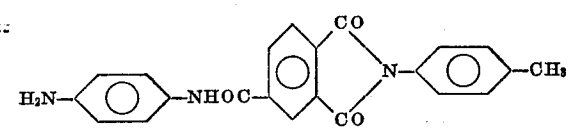
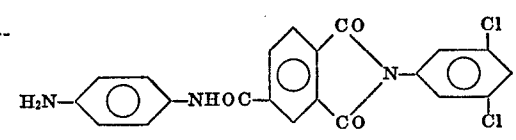
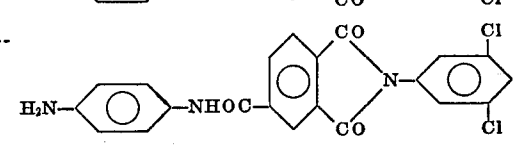
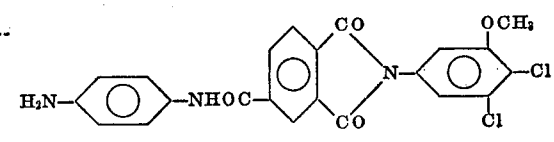
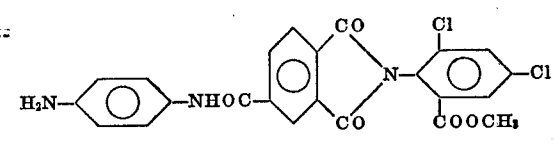
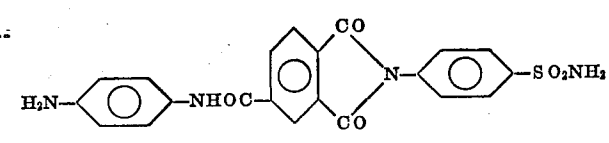
Column III indicates the shade of a coating prepared with the pigment obtained.

Ex.	I	II	III
125			Red.
126	Same as above		Bluish red.
127	do		Red.
128	do		Red.
129	do		Orange.
130	do		Red.
131			Red.
132		Same as above	Red.
133			Red.
134		Same as above	Red.
135		do	Red.

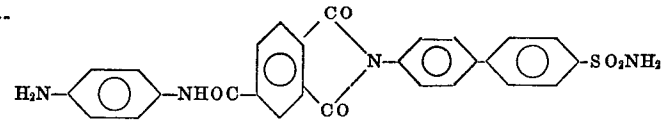
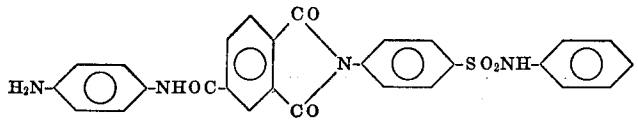
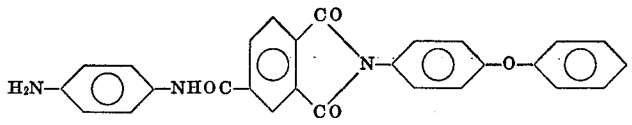
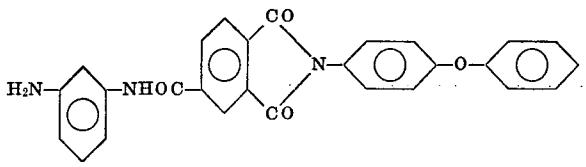
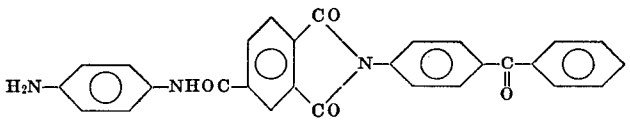
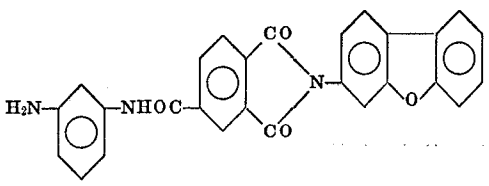
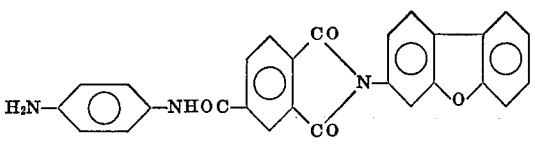
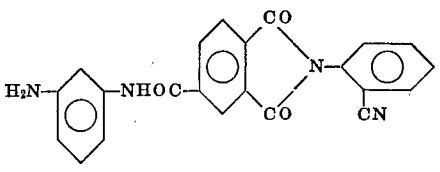
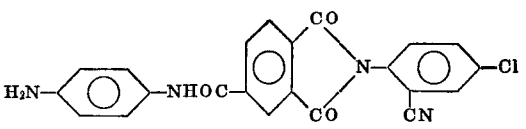
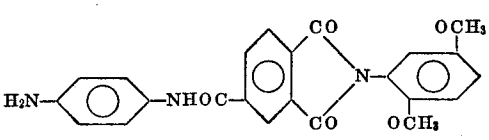
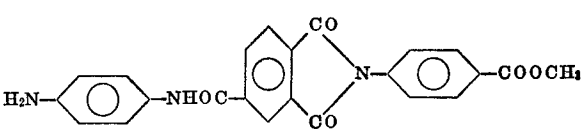
TABLE—Continued

Ex.	I	II	III
136			Bluish red.
137	Same as above		Brownish red.
138	do		Red.
139	do		Orange.
140	do		Red.
141	do		Red.
142	do		Brownish rd. e-
143	do		Bluish red.
144	do		Brownish red.
145	do		Red.

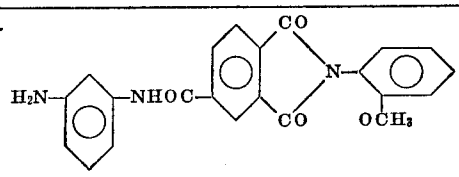
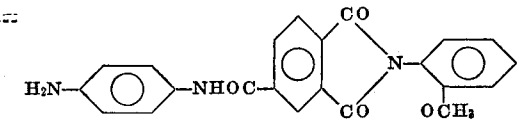
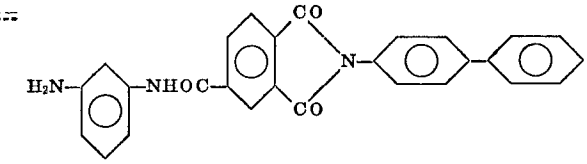
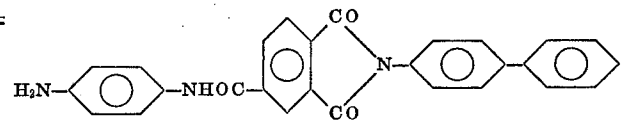
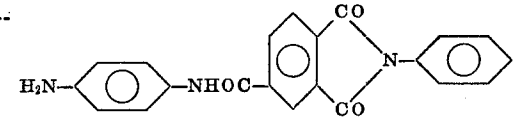
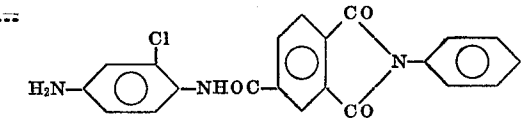
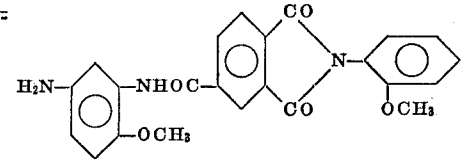
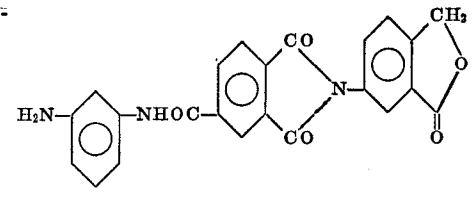
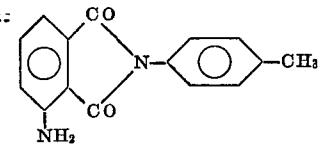
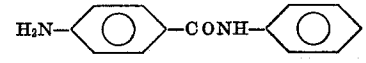
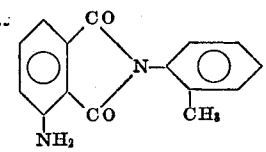
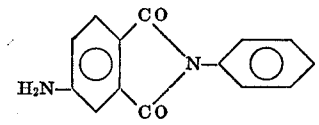
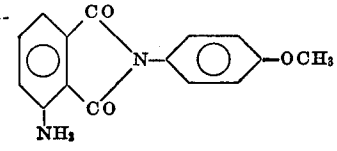
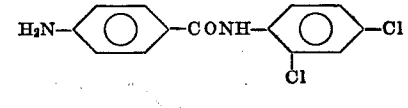
TABLE—Continued

Ex.	I	II	III
146			Red.
147	Same as above		Red.
148	do		Red.
149	do		Red.
150	do		Yellowish red.
151	do		Do.
152	do		Do.
153	do		Do.
154	do		Do.
155	do		Red.
156	do		Yellowish red.
157	do		Red.

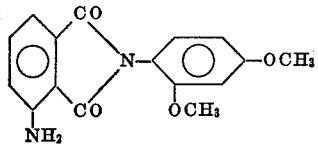
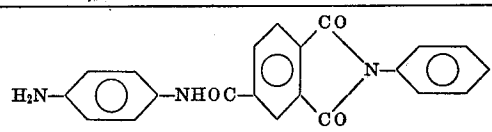
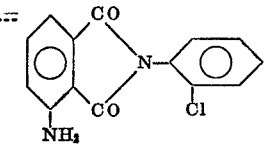
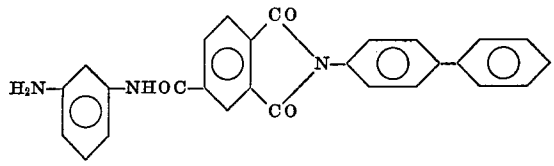
TABLE—Continued

Ex.	I	II	III
158	Same as Example 136		Red.
159	do		Red.
160	do		Red.
161	do		Red.
162	do		Yellowish red.
163	do		Red.
164	do		Red.
165	do		Yellowish red.
166	do		Do.
167	do		Red.
168	do		Yellowish red.

TABLE—Continued

Ex.	I	II	III
169	Same as Example 136		Red.
170	do		Yellowish red.
171	do		Orange.
172	do		Yellowish red.
173	do		Red.
174	do		Red.
175	do		Violet.
176	do		Red.
177			Red.
178			Yellowish red.
179			Red.

TABLE—Continued

Ex. No.	I	II	III
180			Red.
181			Orange.

EXAMPLE 182

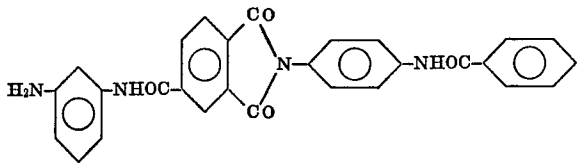
288 parts of the dye obtained by coupling diazotized N-phenyl-3-aminophthalimide with 2-hydroxynaphthoic acid-(3) is heated for five hours at 110° to 120° with 2600 parts of o-dichlorobenzene, 260 parts of thionyl chloride and 8 parts of dimethylformamide while stirring.

After the reaction mixture has been cooled, the uniformly crystalline azo dye monocarboxylic acid chloride is isolated by suction filtration and washed with 200 parts of o-dichlorobenzene, then with 1000 parts of benzene and then with 1000 parts of cyclohexane.

After drying at 80° in vacuo, 266 parts of a red crystal powder is obtained.

Analysis.—Calculated: Cl=7.8%. Found: Cl=7.6%.

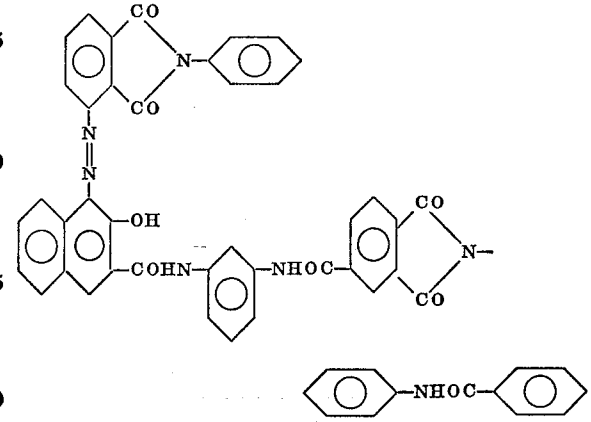
22.8 parts of the azo dye carboxylic acid chloride thus obtained is stirred in 500 parts of N-methylpyrrolidone-(2); then 28.5 parts of the finely powdered amine having the formula:



is added and the whole is heated for five hours at 140° to 150°. The sparingly soluble pigment which is thus deposited in finely crystalline form is cooled to 80°, suction filtered and washed with N-methylpyrrolidone-(2) and then with cold methanol until the filtrate which runs away is clear. The pigment can be improved by boiling it up for two hours with methanol or another solvent or stirring it at room temperature.

After drying at 80° in vacuo, 29 parts of an orange red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film, sheeting and surface coatings are colored orange red shades having very good fastness to light, migration and overcoating.

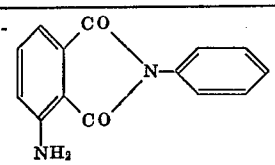
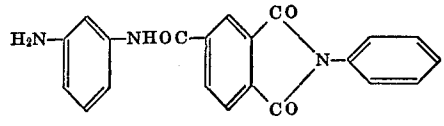
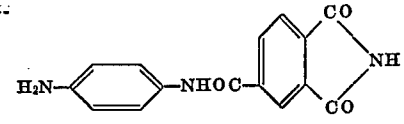
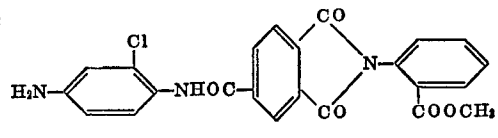
The pigment has the formula:



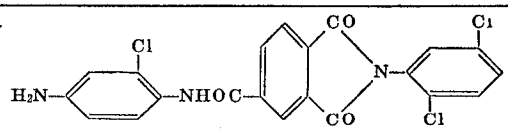
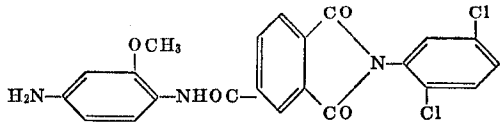
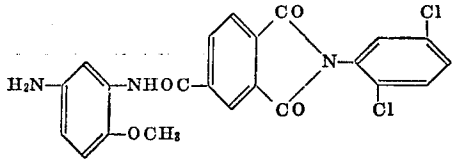
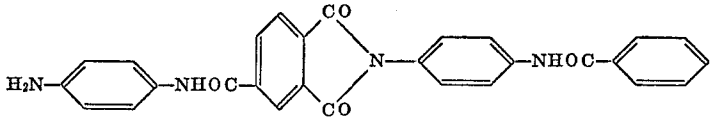
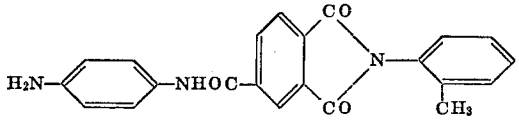
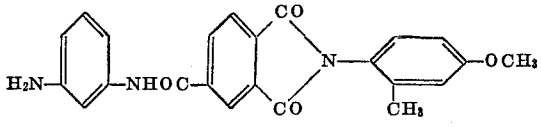
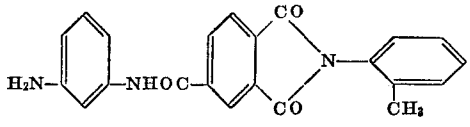
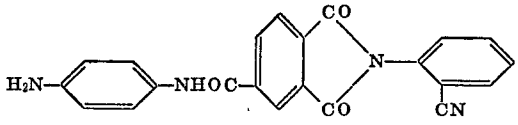
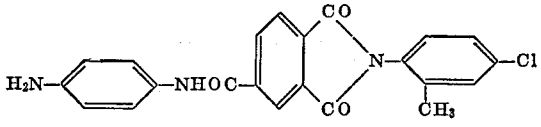
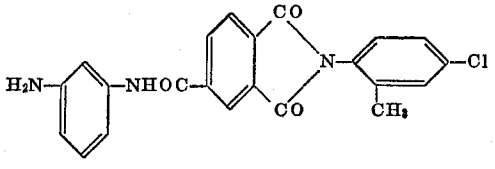
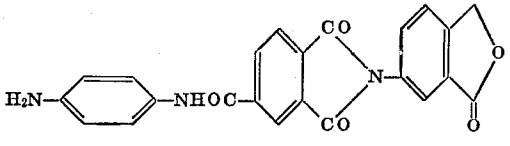
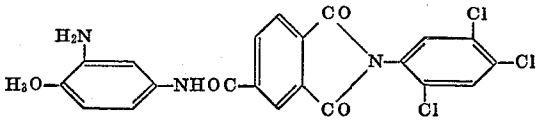
Analysis.—Calculated: N=10.95%. Found: N=11.0%.

Other pigments are obtained with the components in the following Table by coupling the diazo compound of an amine specified in column I, with 2-hydroxynaphthoic acid-(3) and converting the monoazo dye carboxylic acid obtained into its acid chloride which is then condensed with an amine specified in column II.

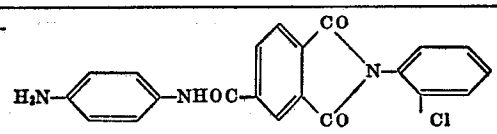
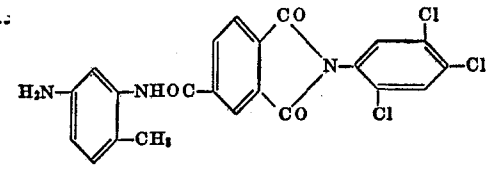
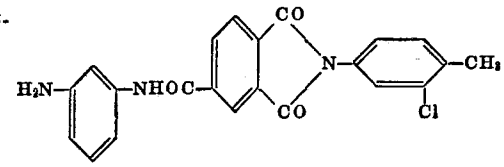
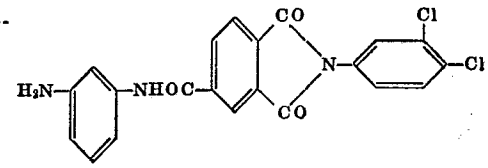
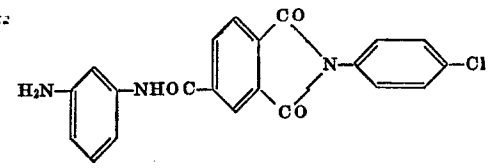
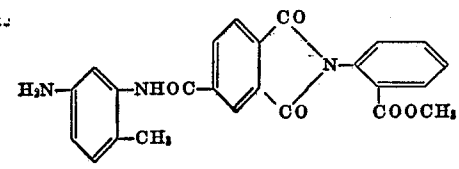
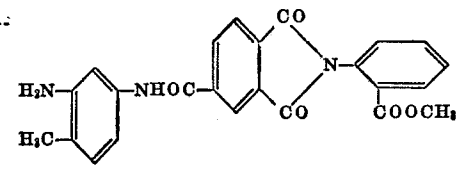
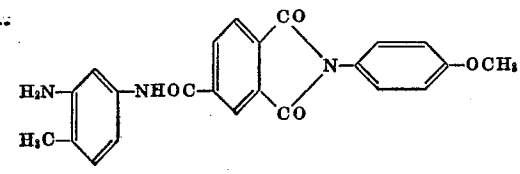
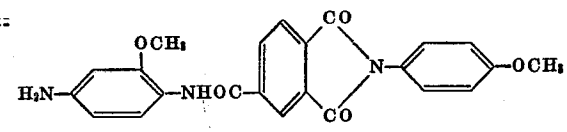
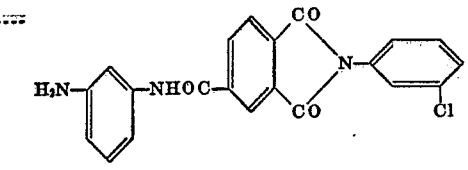
Column III indicates the shade of coatings prepared with the pigment obtained.

Ex. No.	I	II	III
183			Red.
184	Same as above		Bluish red.
185	do		Red.

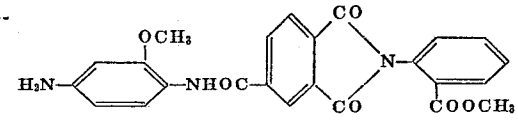
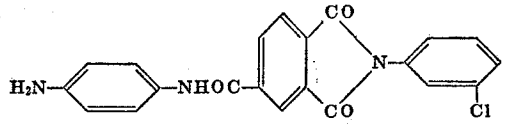
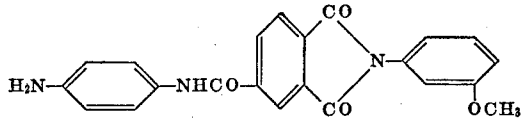
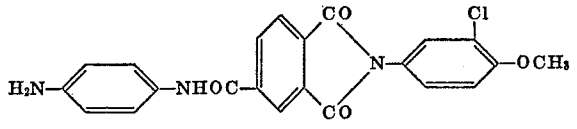
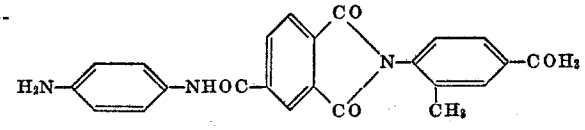
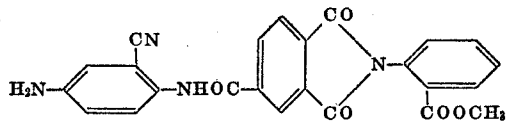
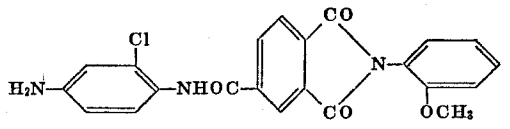
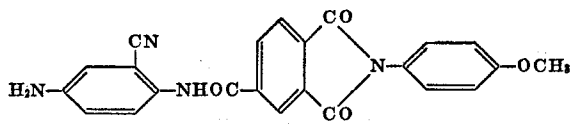
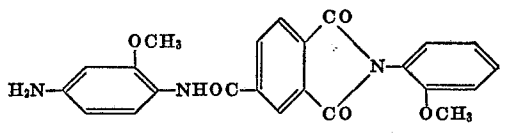
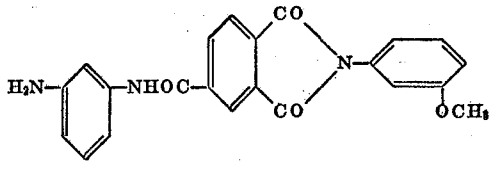
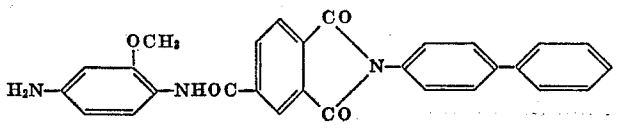
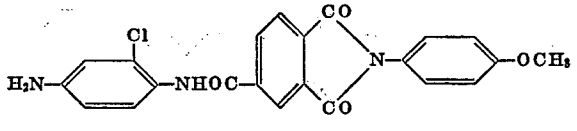
TABLE—Continued

Ex. No.	I	II	III
186	Same as Example 183		Red.
187	do		Chestnut.
188	do		Do.
189	do		Red.
190	do		Red.
191	do		Yellowish red.
192	do		Red.
193	do		Chestnut.
194	do		Red.
195	do		Orange.
196	do		Red.
197	do		Red.

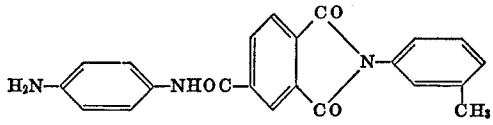
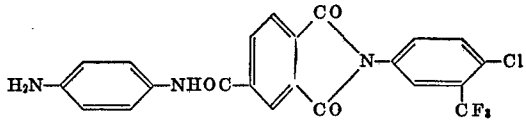
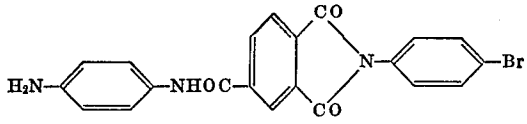
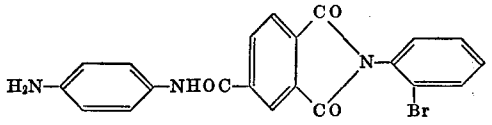
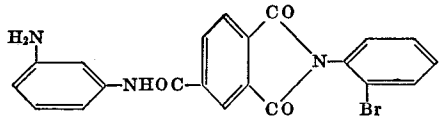
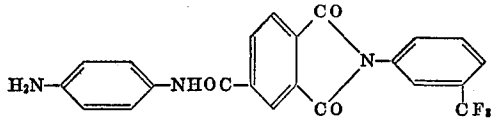
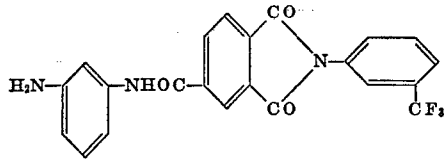
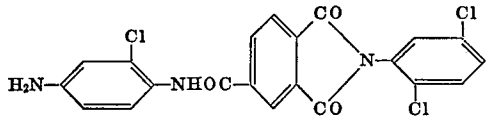
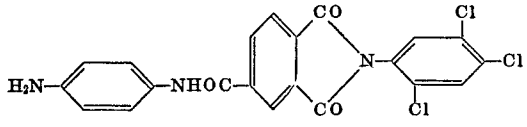
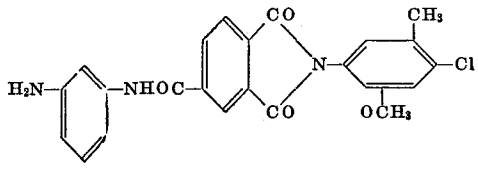
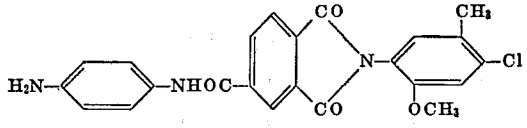
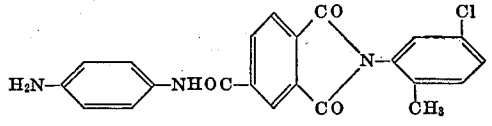
TABLE—Continued

Ex. No.	I	II	III
198	Same as Example 183		Red.
199	do		Red.
200	do		Red.
201	do		Red.
202	do		Red.
203	do		Yellowish
204	do		Do.
205	do		Orange.
206	do		Brown.
207	do		Red.

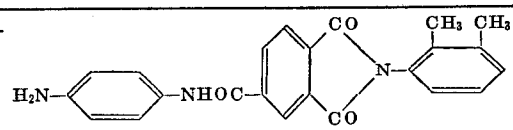
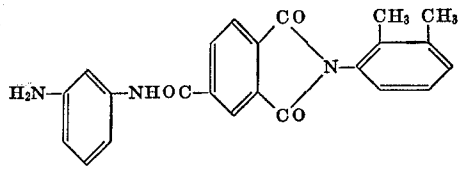
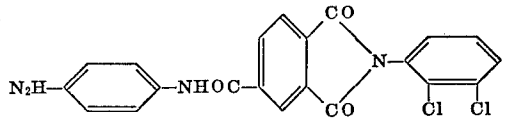
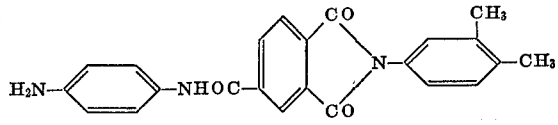
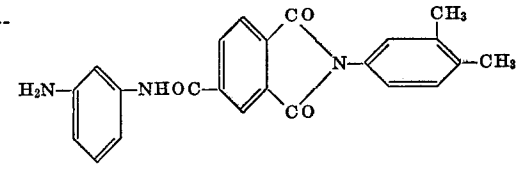
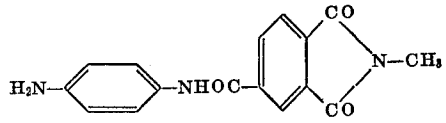
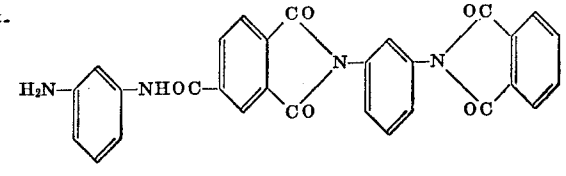
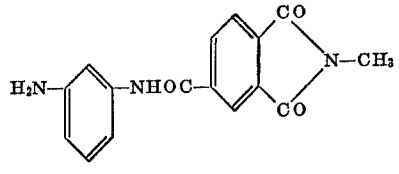
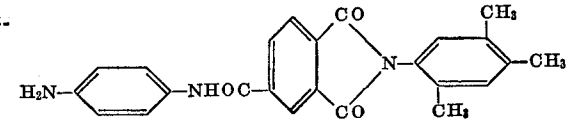
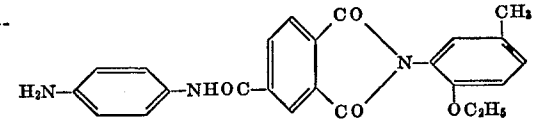
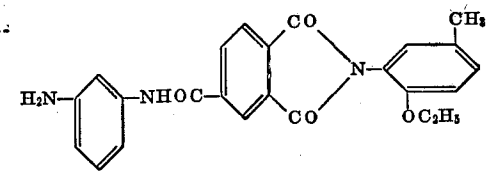
TABLE—Continued

Ex. No.	I	II	III
208	Same as Example 183		Brown.
209	do		Red.
210	do		Red.
211	do		Red.
212	do		Bluish red
213	do		Red.
214	do		Red.
215	do		Red.
216	do		Chestnut.
217	do		Red.
218	do		Brown.
219	do		Red.

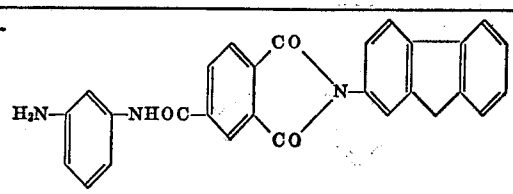
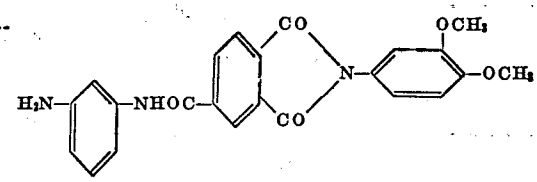
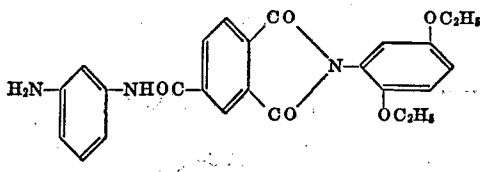
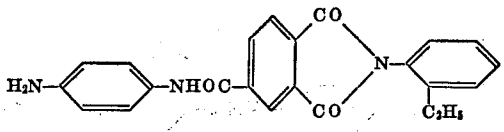
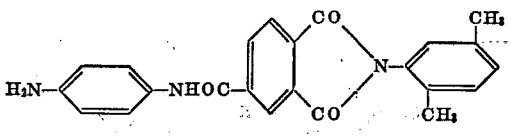
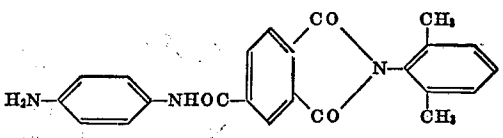
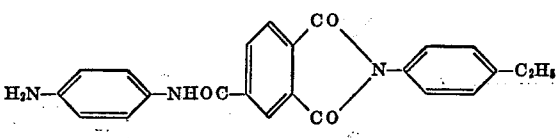
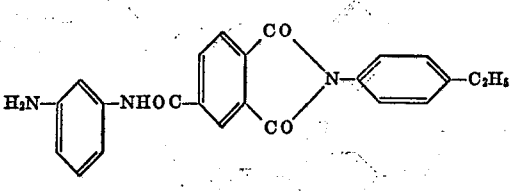
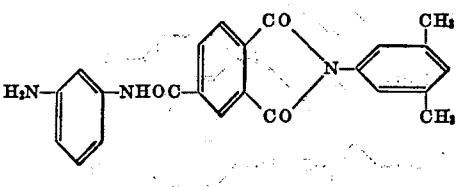
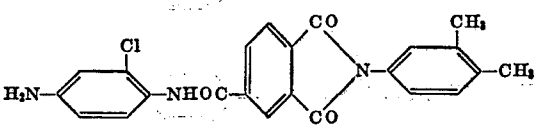
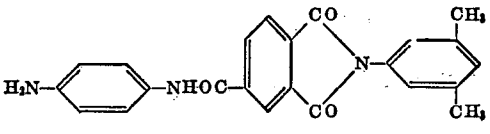
TABLE—Continued

Ex. No.	I	II	III
220	Same as Example 183		Red.
221	do		Red.
222	do		Red.
223	do		Red.
224	do		Red.
225	do		Red.
226	do		Red.
227	do		Red.
228	do		Red.
229	do		Orange.
230	do		Red.
231	do		Red.

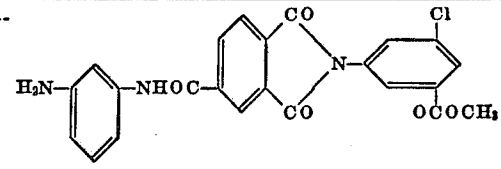
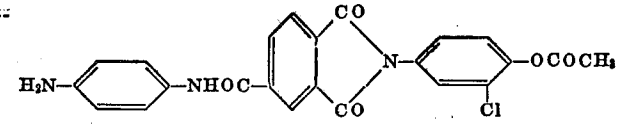
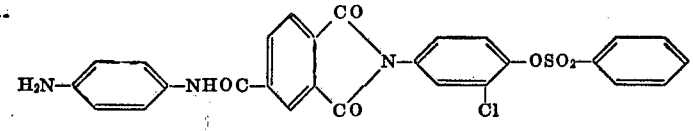
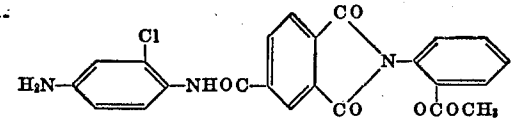
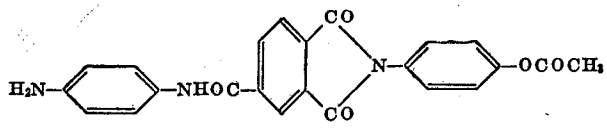
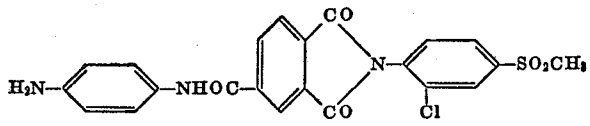
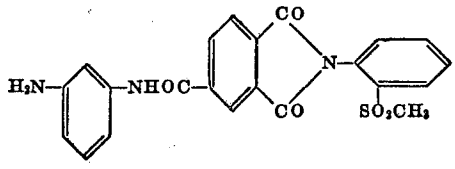
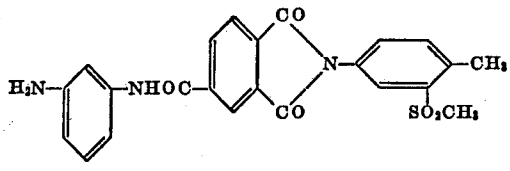
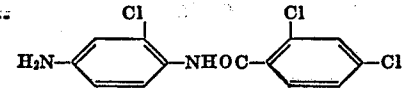
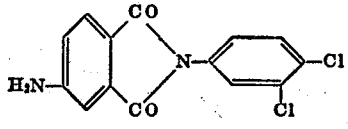
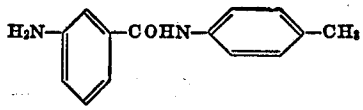
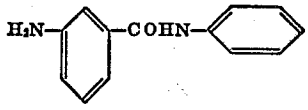
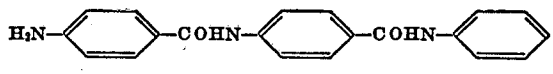
TABLE—Continued

Ex. No.	I	II	III
232	Same as Example 183		Red.
233	do		Orange.
234	do		Red.
235	do		Red.
236	do		Yellowish red.
237	do		Red.
238	do		Yellow.
239	do		Orange.
240	do		Red.
241	do		Red.
242	do		Red.

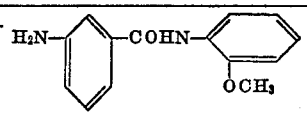
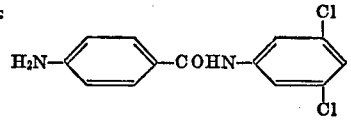
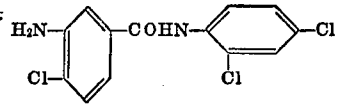
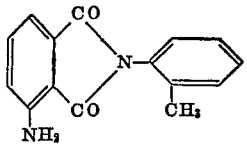
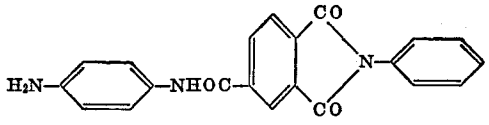
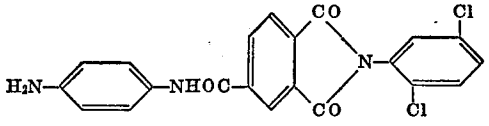
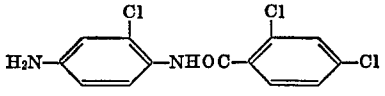
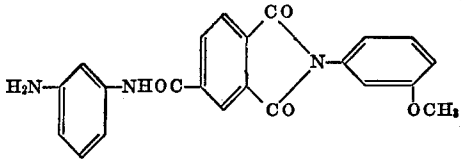
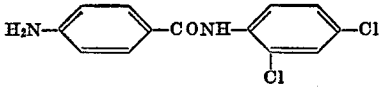
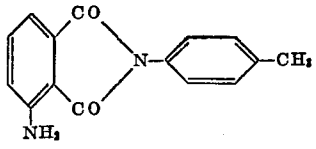
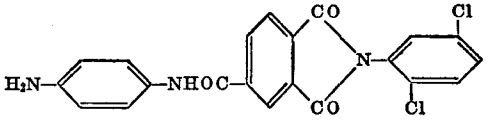
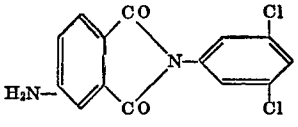
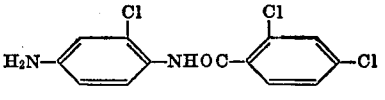
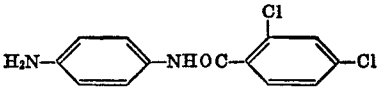
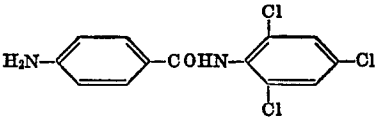
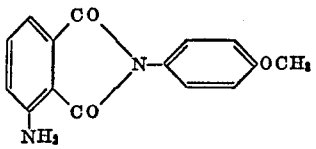
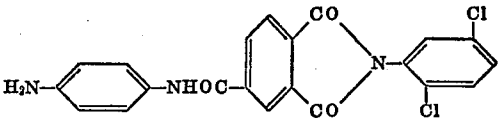
TABLE—Continued

Ex. No.	I	II	III
243	Same as Example 183		Red.
244	do		Red.
245	do		Red.
246	do		Red.
247	do		Red.
248	do		Brown red.
249	do		Red.
250	do		Yellowish red.
251	do		Red.
252	do		Red.
253	do		Red.

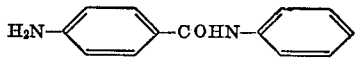
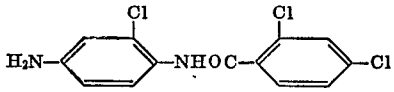
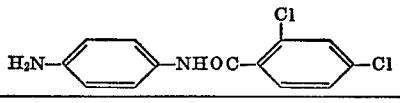
TABLE—Continued

Ex. No.	I	II	III
254	Same as Example 183		Red.
255	do		Red.
256	do		Red.
257	do		Red.
258	do		Red.
259	do		Red.
260	do		Red.
261	do		Red.
262	do		Red.
263	do		Chestnut.
264	do		Yellowish red.
265	do		Red.
267	do		Yellowish red.

TABLE—Continued

Ex. No.	I	II	III
268	Same as Example 183		Red.
269	do		Orange.
270	do		Red.
271			Red.
272	Same as above		Red.
273	do		Red.
274	do		Red.
275	do		Yellowish red.
276			
277	Same as above		Bluish red.
278	do		Red.
279	do		Red.
280	do		Orange.
281			Red.

TABLE—Continued

Ex. No.	I	II	III
282	Same as Example 281		Red.
283	do		Bluish red.
284	do		Red.

EXAMPLE 1

Use in coating compositions

5 parts of the dye obtained according to Example 119 and 95 parts of a baking lacquer mixture (for example 70% of coconut alkyd resin, 60% in xylene, and 30% of melamine resin, about 55% in a mixture of butanol and xylene) are ground in an attrition mill. After application to a substrate and baking for thirty minutes at 120° brilliant full shade coatings are obtained with very good fastness to light and overcoating.

Brilliant white brightening effects are achieved by adding, for example, TiO_2.

Similar coatings in the specified shades are obtained by using the pigments described in the other Examples.

EXAMPLE 2

Use in plastics

Transparent colorations of polystyrene having very good fastness to light are obtained by incorporating 0.05 part of the dye obtained according to Example 1 in 100 parts of polystyrene. Coloration is carried out at 190° to 220° in an extruder.

Polystyrene colorations having good hiding power are obtained analogously by incorporating 0.2 part of the abovementioned dye and 1.0 part of TiO_2 into 100 parts of polystyrene.

Similar results are obtained when the pigments from the other Examples are used.

EXAMPLE 3

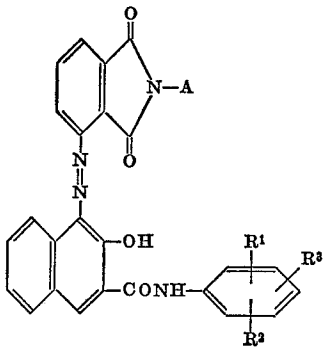
Use in printing inks

5 parts of the dye obtained according to Example 26, 30 to 40 parts of resin (for example rosin modified with phenol-formaldehyde) and 65 to 55 parts of toluene are intimately mixed in a dispersing unit. A toluene intaglio printing ink having excellent light fastness and outstanding brilliance is obtained.

When the pigments from the other Examples are used, printing inks having similar properties and the specified shades are obtained.

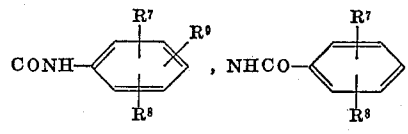
We claim:

1. An azo pigment of the formula:

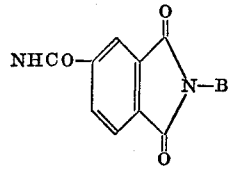


in which

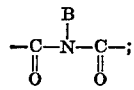
R^1 is



or



R^2 is hydrogen, chloro, bromo, methyl, methoxy, ethoxy, cyano, carbomethoxy, methylsulfonyl, carbamoyl, N - phenylcarbamoyl, N - chlorophenylcarbamoyl, N-methylphenylcarbamoyl, N-methoxyphenylcarbamoyl, N-dichlorophenylcarbamoyl;



R^3 is hydrogen, chloro, methyl, methoxy or ethoxy;

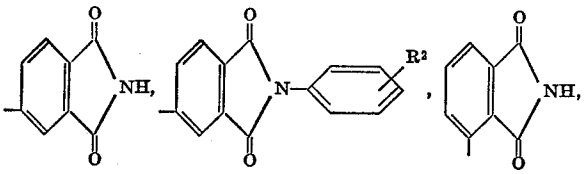
R^7 is hydrogen, fluoro, chloro, methyl, ethyl, methoxy, ethoxy, carbomethoxy, carbamoyl, sulfamoyl, N-phenyl-sulfamoyl or cyano;

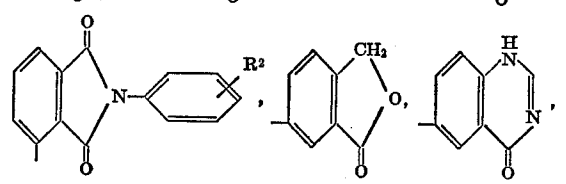
R^8 is hydrogen, chloro, methyl, methoxy or ethoxy;

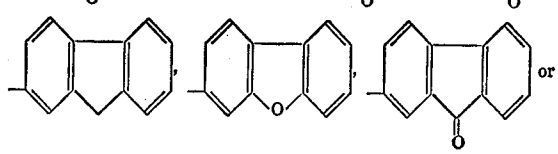
R^9 is hydrogen, chloro, methyl or methoxy;

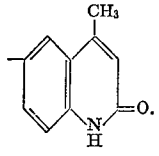
A is phenyl, or phenyl substituted by chloro, cyano, methyl, ethyl, methoxy, ethoxy, carbomethoxy or carboethoxy, naphthyl; or diphenyl; and

B is hydrogen; methyl, phenyl or phenyl substituted by chloro, bromo, methyl, ethyl, methoxy, ethoxy, phenoxy, chlorophenoxy, phenyl, benzoyl, cyano, carbomethoxy, carbamoyl, sulfamoyl, acetylamino, benzoylamino, chlorobenzoylamino, methylbenzoylamino or nitro; naphthyl; chloronaphthyl; or one of the radicals having the formula

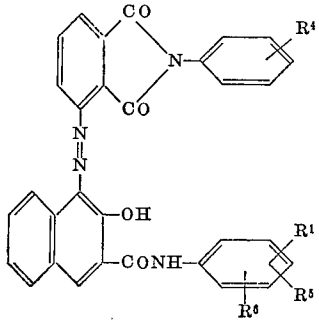








2. A dye as claimed in claim 1 of the formula:



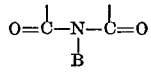
in which

R^4 denotes hydrogen, chloro, methyl, ethyl, methoxy, ethoxy or phenyl;

R^5 denotes hydrogen, chloro, cyano, methyl or methoxy;

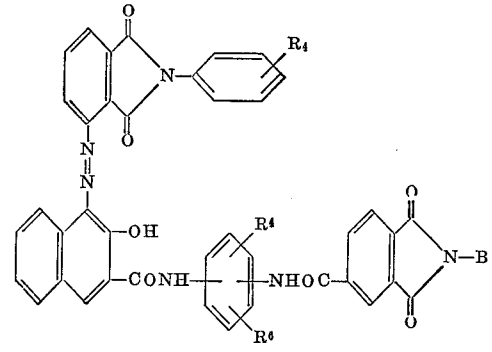
R^6 denotes hydrogen, chloro, methyl or methoxy; and

R^1 and R^5 together may denote the radical of the formula



R^1 and B having the meanings given in claim 1.

3. A dye as claimed in claim 1 of the formula:



in which B, R^4, R^5 and R^6 are meanings given in claim 1.

References Cited

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FLOYD D. HIGEL, Primary Examiner

U.S. Cl. X.R.

8—4; 106—23, 288 Q, 300, 308 Q; 117—138.8 UA; 260—41 B, 41 C, 154, 155, 156, 326 D, 326 N

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,825,527

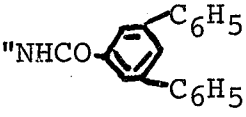
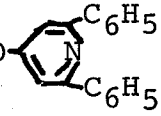
DATED : July 23, 1974

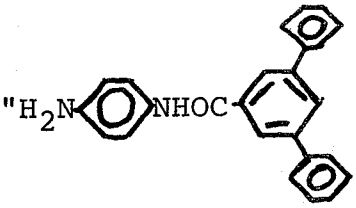
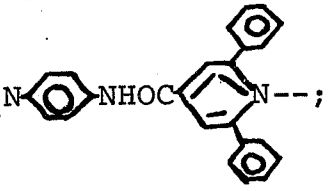
INVENTOR(S) : GUENTHER RUIDER and PETER DIMROTH

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, in the heading, insert--Claims Priority, Application German, December 4, 1970, P 20 59 708.4--

Column 2, line 61, delete "$CONH_6C_4Br$" and substitute--$CONHC_6H_4Br$--;

Column 3, line 25, delete "  ," and substitute--  ,--;

Column 10, line 25, delete "  " and substitute--  --;

Column 17, Example 78, delete "CONH" and substitute--COHN--;

UNITED STATES PATENT AND TRADEMARK OFFICE

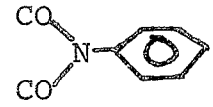
CERTIFICATE OF CORRECTION

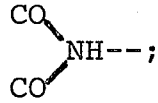
PATENT NO. : 3,825,527

DATED : July 23, 1974

INVENTOR(S) : GUENTHER RUIDER and PETER DIMROTH

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 22, Example 103, delete "  "

and substitute--  --;

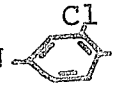
Column 37, Example 180, delete "OCH_3", at the end of the formula;

Column 40, Example 186, delete "  "

and substitute--  --;

Column 42, Example 203, delete "Yellowish" and substitute--Yellowish Red--;

Column 42, Example 204, delete "Do." and substitute--Yellowish Red--;

Column 54, Example 271, second formula, delete "  " and substitute--  --;

Column 54, Example 276, far right side insert

Signed and Sealed this

twentieth Day of January 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks